

PATENT SPECIFICATION

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(54) SELF-CURING EPOXY RESINS

(71) I, HERBERT KOELBEL, a citizen of Germany of Limonenstrasse 14, West Berlin, Germany, do hereby declare the invention for which I pray that a patent may be granted to me and the method by which it is to be performed to be particularly described in and by the following statement:—

5 The present invention relates to the manufacture of self-curing epoxy resins which contain two epoxy groups and two masked isocyanate groups per molecule, such that the compound which blocks the isocyanate can react with epoxy groups. The term "masked isocyanates" is to be understood here as meaning addition compounds of isocyanates and compounds containing hydroxyl groups which, by raising the temperature, are split back into their starting compounds.

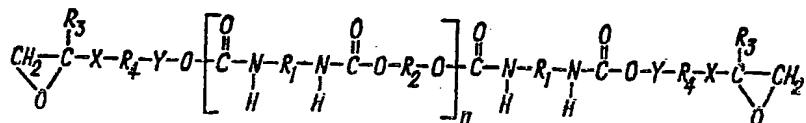
10 Epoxy resin products are known which can be converted into the insoluble and infusible state solely by raising the temperature and without the addition of hardeners. Such epoxy resin products already contain reactive groups, such as carboxyl groups (French Patent No. 1.116.228; C.A. 1957, 6.909), or amino groups (US Patent No. 3.014.895; C.A. 56, 8932 b; Brit. Pat. 814.511; C.A. 54, 17.434 h). The epoxy resin products, however, are not storable over lengthy periods of time.

15 On the other hand, epoxy resin products which contain aliphatic hydroxyl groups as curing constituents are very inactive. They cure only at temperatures around 200°C to give brittle, infusible products (Kunststoffrundschau 15 [4] (1969), page 233). Also resins obtained by the reaction of bisphenols with a mixture of epichlorohydrin and halocarboxylic acids in an alkaline medium require curing temperatures of around 200°C (DBP 964.989).

20 It is also possible to obtain self-curing epoxy resin products by precondensing an epoxy resin product with compounds such as amines, phenols, phenol resins (E. Narracott: Brit. Plast. 28 253—6 (1955) from C.A., 51 760 b) or phenol alcohols by a partial reaction only (Lunkiewitz, Instytut Przemyslu Drobnegoi Rzemiosla; Pol 46 651). Here to, curing to form insoluble and infusible products takes place at temperatures between 150 and 250°C.

25 It has now been discovered that epoxy resin products which contain on average two epoxy groups and two masked isocyanate groups per molecule, can be converted into the insoluble and infusible state solely by raising the temperature if the protective group of the isocyanate is able to react with the epoxy ring of the epoxy resin product.

30 The present invention provides an epoxy resin of the formula:



(I)

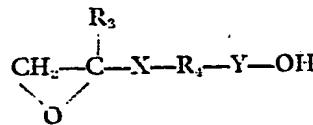
35 in which R_1 represents the residue, after removal of two $-\text{NCO}$ groups, of a diisocyanate and is inert towards epoxy groups, R_2 represents the residue, after removal of two $-\text{OH}$ groups, of a dihydric phenol and is inert towards isocyanate and epoxy groups, R_3 , R_4 , X and Y represent radicals which are inert towards isocyanate and

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epoxy groups and X and Y can also represent valence bonds, and n is greater than 0. Preferably n is less than 5.

The epoxy resin of the formula I is prepared by reacting a dihydric phenol of formula: HO—R₂—OH with a diisocyanate of formula: OCN—R₁—NCO and an epoxy alcohol of formula:



The reaction can be carried out according to known techniques. For example, 2 mols of the organic diisocyanate can be reacted in an inert solvent (e.g. benzene, xylene or dioxan) with 1 mol of the dihydric phenol. The reaction can be carried out, for example, over 2 to 10 hours at 100°C or by heating for a longer period of time at a lower temperature with thorough stirring.

It is advisable to carry out the reaction in an inert atmosphere (e.g. dry nitrogen). The reaction speed of the addition of the phenol to the isocyanate can be increased by means of suitable catalysts.

The resulting solution of a polyurethane containing isocyanate groups can then be reacted at temperatures between 60°C and 120°C with the epoxy alcohol to yield an epoxy resin product of the formula (I). In this stage, 2 mols of the epoxy alcohol are used per 1 mol of the polyurethane containing isocyanate groups.

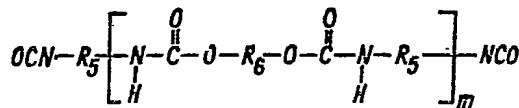
It is also possible, however, to carry out the reaction in such a way that 2 mols of the organic diisocyanate are reacted in an inert solvent with 2 mols of the epoxy alcohol at temperatures between 60°C and 100°C. The resulting epoxy urethane which contains isocyanate groups can then subsequently be reacted with 1 mol of the dihydric phenol.

It is also possible to vary the molar ratio of the three reactants (epoxy alcohol, diisocyanate, dihydric phenol) within wide limits. If the molar amount of dihydric phenol is increased and the molar amount of the epoxy alcohol is simultaneously decreased, epoxy resin products are obtained in which the value of n in the formula (I) is on average greater than 1. On the other hand, if the amount of dihydric phenol is decreased and the amount of the epoxy alcohol increased, epoxy resin products are obtained in which n in the formula (I) is less than 1.

Triisocyanates and polyphenols with more than 2 hydroxy groups or mixtures of various polyisocyanates and various polyphenols may also be used.

The diisocyanates may be a commercial organic diisocyanate, a polyurethane which contains isocyanate groups, or a masked derivative of one of these products. The polyurethanes which contain isocyanate groups can be obtained, for example, by reacting isocyanates with diols (e.g. butane-diol, butene-diol or tricyclodecane-diol), polyalkyl ether glycols (e.g. diethylene glycol, triethylene glycol, branched polypropylene glycols such as Desmophen 3400, Desmophen 3500 (registered trade mark of Bayer AG., Leverkusen)), aryl ether glycols (e.g. reaction products of ethylene oxide, propylene oxide, styrene oxide and other monoepoxides with dihydric phenols, for example, hydroquinone, bisphenol A, dihydroxynaphthalenes, anthrahydroquinone, or hydrogenation products thereof), short-chain polyesters which contain hydroxyl groups (e.g. Desmophen 1000, Desmophen 1100, Desmophen 2100 (registered trade mark) of Bayer AG., Leverkusen)) or short-chain polyurethanes which contain hydroxyl groups.

Diisocyanates of the formula:

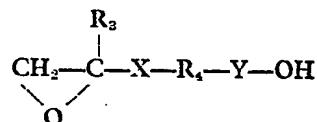


in which R₅ represents an aliphatic or aromatic radical, R₆ represents the residue, after removal of two —OH groups, of an aliphatic diol, polyalkyl ether diol, polyalkylaryl ether diol, polyester diol or polyurethane diol, and m is 0 or an integer, are particularly suitable.

The dihydric phenol may be a dihydroxybenzene, dihydroxynaphthalene or dihydroxyanthracene or a bisphenol (i.e. a compound whose two hydroxyl groups are

located on two isolated aromatic radicals which are bonded to each other directly or via bridge atoms) and the aromatic rings may be alkylated or halogenated.

The epoxy alcohol may be any compound which contains one aliphatic hydroxyl group and one epoxy group per molecule, and which corresponds to the formula:



wherein X, Y, R₃ and R₄ are as defined above. Epoxy alcohols in which R₃ represents a methyl or phenyl radical or, preferably a hydrogen atom, R₄ represents an aliphatic, cycloaliphatic or araliphatic radical, X represents a heteroatom, a valence bond, a hydrocarbon bridge which may also contain heteroatoms (e.g. ether bridges), ester or urethane groups and Y represents a valence bond, a hydrocarbon bridge which may also contain heteroatoms, ester or urethane groups, are particularly suitable. Epoxy alcohols, such as epoxycyclohexanol, may also be used.

The epoxy resins of the invention possess a number of noteworthy advantages compared with the known self-curing resins. A number of the known self-curing epoxy resins contain as hardeners, for example, free amino, carboxyl or hydroxyl groups. If the resins are stored for some period of time, these reactive groups lead to a cross-linking of the individual molecules. After a time, the resins are completely cured and can no longer be used. On the other hand, known self-curing epoxy resins which are storable are so inactive that curing temperatures of approx. 200°C are required. The resulting cured products are badly discoloured by the high curing temperature and are frequently very brittle. In comparison, in the resins of this invention the hardener (dihydric alcohol) is "blocked" at room temperature by the isocyanate. If the resin is heated, the phenol-isocyanate bond splits and the liberated phenol can react with the free epoxy groups. The resulting free isocyanate group enhances the curing.

In the resins of the present invention, this cross-linking occurs at temperatures between 80°C and 120°C. Due to the mild curing conditions, the resulting products are colourless or only faintly discoloured.

The present invention also provides a process for the manufacture of cured molded articles, coatings, impregnations or bonds, which comprises curing an epoxy resin of formula (I) by the application of heat and in the absence of hardeners for epoxy resins.

In contrast to most of the known self-curing epoxy resins, the products obtained from the epoxy resins of this invention possess outstanding mechanical properties. Whereas the resins obtained by self-curing the known epoxy resins are markedly brittle, the cured products described herein possess great impact strengths (up to more than 70 kpcm/cm²; assessed according to DIN 53 453; test article: standard small test specimen). Due to their good mechanical properties and their good bond strength, they can be used, moreover, as adhesives and as stoving lacquers of high elasticity.

Example 1

40 0.4 Mol of hexamethylene diisocyanate is dissolved in 100 ml of absolute benzene and the solution heated to 100°C. While stirring thoroughly, 0.2 mol of bisphenol A is added to the reaction solution. Five hours after the bisphenol has dissolved, 0.2 mol of epoxypopropanol dissolved in 50 ml of absolute benzene is slowly added dropwise at a bath temperature of 60°C. Eight hours after completion of addition of the epoxy alcohol, the solvent is stripped off in a rotary evaporator. The residual epoxy resin product melts at approx. 60°C.

Curing conditions: 8 hours at 100°C and 17 hours at 150°C.

45 Impact strength: 30.8 kpcm/cm² (DIN 53 453; test articles: standard small test specimen).

50 Dimensional stability under heat (Martens): 62°C.

Example 2

A. Procedure as in Example 1, but using tetrabromobisphenol A instead of bisphenol

55 Curing conditions: 17 hours at 150°C.

Impact strength: 30.0 kpcm/cm².

Dimensional stability under heat (Martens): 104°C.

Ball indentation hardness: 1450 kp/mm².

Example 3

Procedure as in Example 1, but using 1,6-dihydroxynaphthalene instead of bisphenol A.

5 Curing conditions: 17 hours at 120°C.

Impact strength: 47.5 kpcm/cm².

Dimensional stability under heat (Martens): 64°C.

Example 4

Procedure as in Example 1, but using 1,7-dihydroxynaphthalene instead of bisphenol A.

10 Curing conditions: 17 hours at 180°C.

Impact strength: 52 kpcm/cm².

Dimensional stability under heat (Martens): 66°C.

Example 5

Procedure as in Example 1, but using pyrocatechol instead of bisphenol A.

15 Curing conditions: 17 hours at 150°C.

The moulded articles obtained are distinguished primarily by their very good light transmittance.

Impact strength: 17 kpcm/cm².

Dimensional stability under heat (Martens): 56°C.

Example 6

20 37 Grams of hexamethylene-diisocyanate are dissolved in 50 ml of absolute benzene, 4.6 g of bisphenol A are added and the solution is heated for 4 hours to 100°C. The reaction solution is cooled to 80°C and to it are added 29.6 g of epoxy-propanol dissolved in 50 ml of absolute benzene. The reaction is completed in 6 hours at a temperature of 60°C. The solvent is then removed in vacuo to leave as residue the completely colourless epoxy resin product, which melts at approx. 60°C.

25 Curing conditions: 17 hours at 100°C.

Impact strength: 72 kpcm/cm².

Example 7

30 60.3 Grams of hexamethylene-diisocyanate and 35.8 g of bisphenol A are dissolved in 100 ml of absolute benzene. The mixture is heated for 5 hours to 100°C, then cooled to 60°C. 3 Grams of triethyleneglycol are added thereto, the mixture is left to stand for 20 hours at 20°C and 26.6 g of epoxypropanol dissolved in benzene are then added dropwise. The reaction mixture is stirred for 5 hours at 20°C, and subsequently for 5 hours at 60°C. The solvent is removed in vacuo.

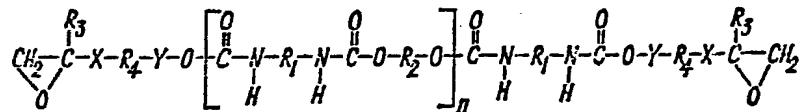
35 Curing conditions: 17 hours at 100°C, and 17 hours at 180°C.

Impact strength: 58.5 kpcm/cm².

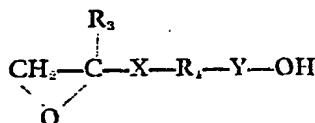
Dimensional stability under heat (Martens): 65°C.

WHAT I CLAIM IS:—

40 1. A process for the manufacture of an epoxy resin of the general formula:



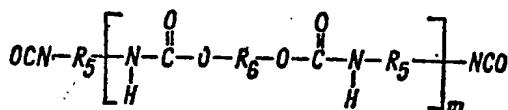
in which R₁ represents the residue, after removal of two —NCO groups, of a diisocyanate and is inert towards epoxy groups, R₂ represents the residue, after removal of two —OH groups, of a dihydric phenol and is inert towards isocyanate and epoxy groups, R₃, R₄, X and Y represent radicals which are inert towards isocyanate and epoxy groups and X and Y can also represent valence bonds, and n is greater than 0, which comprises reacting a dihydric phenol of formula: HO—R₂—OH with a diisocyanate of formula: OCN—R₁—NCO and an epoxy alcohol of formula:



2. A process according to Claim 1, wherein R_3 represents a methyl or phenyl radical or a hydrogen atom, R_4 represents a bivalent aliphatic, cycloaliphatic or araliphatic radical, X represents a hetero atom, a valency bond or a hydrocarbon bridge optionally containing one or more heteroatoms or ester or urethane groups, Y represents a valence bond or a hydrocarbon bridge optionally containing one or more heteroatoms or ester or urethane groups and n is less than 5.

5 3. A process according to Claim 1 or 2, wherein the molar ratio of dihydric phenol:diisocyanate:epoxy alcohol is 1:2:2.

10 4. A process according to Claim 1, 2 or 3, wherein the diisocyanate is a compound of the general formula:



15 in which R_6 represents an aliphatic or aromatic radical, R_5 represents the residue, after removal of two $-\text{OH}$ groups, of an aliphatic diol, polyalkyl ether diol, polyalkylaryl ether diol, polyester diol or polyurethane diol, and m is 0 or an integer.

15 5. A process according to any of Claims 1 to 4, wherein the dihydric phenol is a dihydroxybenzene, a dihydroxynaphthalene or a dihydroxyanthracene, optionally alkylated or halogenated.

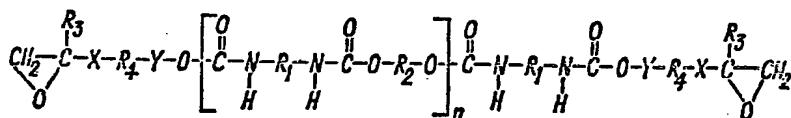
20 6. A process according to any of Claims 1 to 4, wherein the dihydric phenol is a bisphenol, optionally alkylated or halogenated.

7. A process according to Claim 1, substantially as hereinbefore described.

20 8. A process according to Claim 1, substantially as described in any of the Examples.

9. An epoxy resin obtained by a process according to any of the preceding Claims.

10. An epoxy resin of the formula:



25 in which R_1 represents the residue, after removal of two $-\text{NCO}$ groups, of a diisocyanate and is inert towards epoxy groups, R_2 represents the residue, after removal of two $-\text{OH}$ groups, of a dihydric phenol and is inert towards isocyanate and epoxy groups, R_3 , R_4 , X and Y represent radicals which are inert towards isocyanate and epoxy groups and X and Y can also represent valence bonds, and n is greater than 0.

30 11. An epoxy resin according to Claim 10, wherein R_3 represents a methyl or phenyl radical or a hydrogen atom, R_4 represents a bivalent aliphatic, cycloaliphatic or araliphatic radical, X represents a hetero atom, a valency bond or a hydrocarbon bridge optionally containing one or more hetero atoms or ester or urethane groups, Y represents a valence bond or a hydrocarbon bridge optionally containing one or more hetero atoms or ester or urethane groups and n is less than 5.

35 12. An epoxy resin according to Claim 10, substantially as hereinbefore described.

35 13. A process for the manufacture of cured moulded articles, coatings, impregnations or bonds which comprises curing an epoxy resin as claimed in any of Claims 9 to 12 in the absence of hardeners for epoxy resins by the application of heat.

40 14. A process according to Claim 13, wherein the curing is carried out at 80° to 120°C.

15. Cured moulded articles, coatings, impregnations or bonds when obtained by a process according to Claim 13 or 14.

J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square,
Gray's Inn, London, W.C.1.

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